

ATRAZINE AND CARBOFURAN TRANSPORT THROUGH THE VADOSE ZONE IN THE CLAIBORNE AQUIFER RECHARGE AREA

D. D. Bosch, C. C. Truman, R. A. Leonard

ABSTRACT. A 1-ha field plot with a sandy surface soil, located near Plains, Georgia, was studied for three years (from 1993 to 1995) to evaluate pesticide transport in the vadose zone. Vadose zone soil samples were collected 23 times: prior to the initial 1993 pesticide application, each year at approximately 1, 3, 7, 14, 28, and 44 days after pesticide application, each fall after harvest, and in the spring of 1995 prior to planting. The samples were analyzed for atrazine, carbofuran, deethylatrazine (DEA), and deisopropylatrazine (DIA). Atrazine and carbofuran in the active root zone (< 100 cm) degraded rapidly. Overall, the higher concentration levels of atrazine, DEA, DIA, and carbofuran were limited to the top 25 cm of the profile and to the period from 1 to 30 days after application. On the average, by 30 days after application 83% of the atrazine and 96% of the carbofuran had degraded. By 44 days after application, virtually all of the pesticides in the top 250 cm of the soil had degraded. Atrazine was found to be more persistent than was carbofuran with a half life approximately twice that for carbofuran. A two-stage model with a variable dissipation rate for the period up to 44 days after pesticide application and a second dissipation rate for periods greater than that was found to fit the data better than a single stage model. For the first 44 days after application, the first-order decay rate with a half life of 12 days was found to fit the field data for atrazine within the soil profile. A first-order decay rate with a half life of approximately 6 days fit the observed carbofuran data best. The dissipation rate decreased rapidly after the first 44 days. When a two-stage dissipation process was assumed, the dissipation rate coefficient decreased from 0.059 to 0.006 (days^{-1}) for atrazine, while for carbofuran it decreased from 0.110 to 0.018 (days^{-1}). Observed levels of the atrazine metabolites DIA and DEA were highest in the top 1 cm of the soil. There appeared to be some movement or creation of the metabolites at lower depths in the profile later in the growing season, but not at large concentrations.

Keywords. Soils, Aquifers, Pesticide transport, Water quality, Atrazine, Carbofuran.

The southern Coastal Plain of the U.S. is a physiographic region with a wide range of soil types and crop management systems. The region's abundant rainfall and long growing season are conducive to intense crop production. Studies conducted by scientists at the Southeast Watershed Research Laboratory (SEWRL) Tifton, Georgia, and the USGS, Georgia District, have revealed significant pesticide and pesticide metabolite concentrations in area aquifers (Bosch et al., 1997; Leonard et al., 1979; Leonard et al., 1988).

The Clayton and Claiborne aquifers of southwestern Georgia are important sources of groundwater, supplying the majority of municipal, industrial, agricultural, and domestic water for the area (McFadden and Perriello, 1983). In this area, the sedimentary deposits in which these

aquifers reside gently dip to the southeast from the central portion of Georgia. These aquifers outcrop and are recharged in a belt trending southwest-northeast through the center of the state (Beck et al., 1985). Because of this, the land use in this area is of great importance to the citizens of South Georgia and North Florida.

Losses of agricultural chemicals from the root zone are important relative to both crop production and environmental quality. When agrichemicals leave the root zone they are no longer available for crop protection and growth and may negatively impact surface or subsurface water quality. Transport of agrichemicals depends on rainfall amount, intensity, and duration, chemical solubility and dissipation properties, soil properties, biological processes, and management practices. A scientific understanding of these processes requires complex well defined research which quantifies each of these factors.

Two pesticides of particular interest are atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) and carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methyl carbamate). Atrazine is widely and extensively used in many parts of the world for the control of a variety of weeds. Carbofuran is an insecticide used for insect, mite, and nematode control in maize and other crops. Reported soil organic carbon sorption coefficients for atrazine range from 38 to 174 (mL g^{-1}) while measured field dissipation half lives range from 18 to 120 days (Hornsby et al., 1996). Field dissipation includes volatilization, degradation, and transformation, and is a function of annual variations in management and climate. Carbofuran is generally

Article was submitted for publication in March 2000; reviewed and approved for publication by the Soil & Water Division of ASAE in September 2000.

Trade names and company names are included for the benefit of the reader and do not imply any endorsement or preferential treatment of the products listed by USDA. All programs and services of the U.S. Department of Agriculture are offered on a nondiscriminatory basis without regard to race, color, national origin, religion, sex, age, marital status, or handicap.

The authors are **David D. Bosch**, ASAE Member Engineer, Research Hydraulic Engineer, **Clinton C. Truman**, Soil Scientist, and **Ralph A. Leonard**, Retired Soil Chemist, USDA-ARS, Southeast Watershed Research Laboratory, Tifton, Ga. **Corresponding author:** D. D. Bosch, Southeast Watershed Research Laboratory, PO Box 946, Tifton, GA 31793, phone: 912.386.3899, fax: 912.386.7294, e-mail: <dbosch@tifton.cpes.peachnet.edu>.

considered more mobile but less persistent. Soil organic carbon sorption coefficients for carbofuran range from 9 to 105 (mL g^{-1}) and measured field dissipation half lives range from 9 to 90 days (Hornsby et al., 1996). Both pesticides are quite mobile in soil, but with fairly rapid decay rates. Surveys conducted by Goodrich et al. (1991) and by USEPA (1990) indicated that atrazine is frequently detected in ground water samples during monitoring studies.

Within the soil, pesticides can be degraded and transformed into other compounds (metabolites). Concerns over total pesticide concentrations, parent and metabolite, are increasing. Initial pesticide studies rarely measured pesticide metabolites. This was largely due to less sensitive analytical instruments and methods, and an inadequate understanding of pesticide transformations. However, we are now aware that health concerns related to metabolites are often as great or greater than those related to parent compounds. Because of the wide use of atrazine, two metabolites of particular interest are deethylatrazine (DEA) (2-amino-4-chloro-6-isopropylaniline-s-triazine) and deisopropylatrazine (DIA) (2-amino-4-chloro-6-ethylamino-s-triazine). Conversions of atrazine into DEA and DIA by soil microorganisms are the main biotic dissipation pathways of atrazine in the soil environment (Jayachandran et al., 1994). DEA is about 10 times more soluble than atrazine (Gaynor et al., 1995) and leaching rates of DEA can exceed those of atrazine (Fermanich et al., 1996). Atrazine can also be transformed through hydrolysis into hydroxyatrazine (2-hydroxy-4-ethylamino-6-isopropylamino-s-triazine). Chlorinated atrazine metabolites possess a similar health risk to that of atrazine (Belluck et al., 1991), and their presence in groundwater has been documented (Adams and Thurman, 1991; Jayachandran et al., 1994; Gaynor et al., 1995). Hydroxyatrazine is more strongly bound to the soil than atrazine, DEA, and DIA, and therefore is less mobile and of less environmental concern than the other compounds (Jayachandran et al., 1994).

The objectives of this study were to:

1. Determine transport and dissipation characteristics of atrazine and carbofuran under conventional agricultural practice.
2. Quantify atrazine transformation into the DEA and DIA metabolites.
3. Relate observed transport and dissipation to soil and climatic conditions.
4. Develop data bases on chemical transport in root and vadose zones to support development and evaluation of individual and linked water quality models.

METHODS

SITE DESCRIPTION AND CHARACTERIZATION

A 1-ha field plot located near Plains, Georgia, was identified to carry out this research (fig. 1). The site is located in the Fall Line Hills geographic province of west-central Georgia (Clark and Zisa, 1976). The water table was approximately 12 m below ground surface. The surface soil is composed of a highly permeable loamy sand or sand (Bosch and West, 1998). While surface runoff was expected to be small, appropriate measures were none the

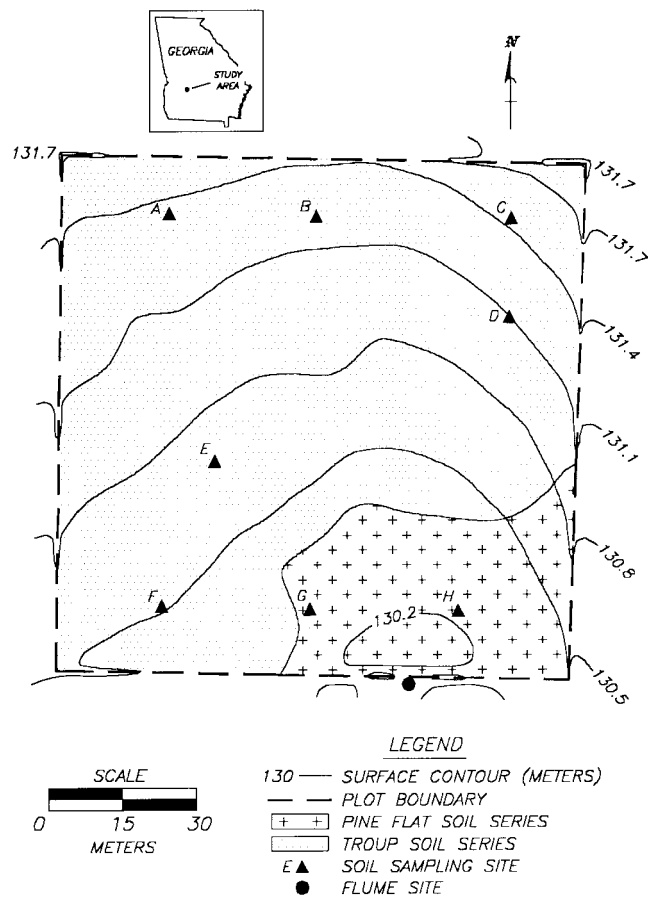


Figure 1—Plot configuration, site locations, and soil definitions.

less taken to measure runoff and capture runoff samples. A soil berm was constructed around the perimeter of the plot to confine runoff. An H-flume (46 cm) was installed in the southeast corner of the plot to measure sediment and chemical transport in the surface runoff. An automatic sampler connected to a depth measurement transducer was used to collect runoff samples. Prior to beginning this study, this plot was not in agricultural production for many years. The plot was surrounded by forested and untilled land, minimizing the likelihood of off-site inputs.

Basic soil texture characterization and classification was done through analysis of samples collected at eight sites located throughout the plot area (fig. 1). Additional samples were collected along a transect from the southeast corner of the plot to the northeast corner for a study which characterized spatial variability (Bosch and West, 1998). Undisturbed core samples were collected from the shallow vadose zone (0 to 150 cm) using a Giddings coring device (Giddings, Inc., Fort Collins, Colo.). The samples were collected within the core barrel in a 7.6-cm-diameter by 12.5-cm-long plexiglass core. Soil-water release curves were determined following the methods of Klute (1986) and saturated hydraulic conductivities were measured using the methods of Klute and Dirksen (1986). Bulk density and porosity was determined after oven drying the soil sample. Additional undisturbed or minimally disturbed core samples were collected from soil pits created at the site and from core samples collected using a drilling rig (Shaw et al., 1999).

SITE MANAGEMENT

The field was in a cropping sequence of summer corn (*Zea Maize* L.) and winter wheat from 1993 through 1995. Following corn harvest in August or early September, wheat was planted in late November to early December. Conventional agricultural management practices were used for tillage, fertilization, planting, and harvest. A center-pivot irrigation system was used. The plot was fertilized for the corn each spring and for the wheat in the fall.

The herbicide atrazine and the insecticide carbofuran were applied separately by a tractor mounted sprayer each year just prior to planting (table 1). The pesticides were surface applied and incorporated approximately 5 cm into the soil. Irrigation was supplied each year immediately after planting to minimize pesticide volatilization losses (table 1). During the crop season, irrigation was applied as needed to prevent water stress. A well tapping a deeper aquifer, vertically isolated from the impacted Claiborne aquifer, provided water to the center-pivot irrigation system. Precipitation measurements were made using a recording tipping bucket rain gage located at the site. The gage recorded 5-min rainfall totals. Irrigation volumes were measured using standard manual rain gages.

SAMPLE COLLECTION

Eight sample sites were selected within the plot (fig. 1). The locations for these sites were selected based upon preliminary soil observations. The sites were selected to sample subsurface soil features which were expected to alter agrichemical transport. It was anticipated that an equal number of sites would be installed in each soil type. However, the Pine Flat soil was not as extensive as was initially believed, and fewer sites were obtained in this soil.

Vadose zone soil samples were collected 23 times: prior to the initial 1993 pesticide application, each year at approximately 1, 3, 7, 14, 28, and 44 days after pesticide application, each fall after harvest, and in the spring of 1995 prior to planting. Soil samples were collected at each of the eight sites (fig. 1). The soil samples were collected using 5-cm-diameter bucket augers during the growing season. The soil samples collected during the growing season were collected to various depths, depending upon where the depth of transport was expected to be. The minimum depth sampled to was 75 cm, at one day after application in 1995, while the maximum depth sampled to during the growing season was 250 cm, at 44 days after application. A sample in the top centimeters of the soil was collected on each sampling date by scraping the soil surface. The top 25 cm was divided into two samples, 12.5 cm each. The remainder of the samples from deeper in the profile were collected in 25 cm intervals down to 100 cm and in 50 cm intervals below that. Samples collected prior to planting and in the fall after the growing

season were collected down to the water table at approximately 12 m. A continuous auger well-drilling machine equipped with a hollow-stem auger and internal split-tube core barrel was used to collect these samples. One sample was collected in the top 15 cm, with additional samples every 30 cm down to the water table. Each sample interval was thoroughly mixed and split into a sample for soil-water determination and a sample for pesticide analysis. All samples for pesticide analysis were frozen until extracted.

ANALYTICAL METHODS

Soil samples were extracted for carbofuran, atrazine, DEA, and DIA. Fifty grams of moist soil was mixed with 150 mL of 1:1 methanol:water, shook for 3 h, and filtered through glass filters after standing overnight. Filtrates were centrifuged as needed for clarity and the volume of the recovered extract measured and reduced overnight under a fume hood to remove most of the methanol. The volume was then brought to 200 mL with deionized water, adjusted to pH 7-7.2 and passed through a preconditioned cyclohexyl solid phase extraction (SPE) column assisted by vacuum. The SPE columns were dried by centrifugation and eluted with 2 mL of methanol. Analysis was either by capillary column gas chromatography (GC) equipped with a nitrogen-phosphorous detector or high pressure liquid chromatography (HPLC). The detection method was selected based upon the expected level of concentration of the compounds in the samples. Carbofuran, atrazine and DEA measurements were made each year of the study. DIA measurements were made in 1994 only. Method detection limits on the HPLC were 0.075 $\mu\text{g kg}^{-1}$ soil for carbofuran, 0.090 $\mu\text{g kg}^{-1}$ soil for atrazine, 0.100 $\mu\text{g kg}^{-1}$ for DEA, and 0.200 $\mu\text{g kg}^{-1}$ DIA. Method detection limits on the GC were 0.050 $\mu\text{g kg}^{-1}$ soil for carbofuran, 0.010 $\mu\text{g kg}^{-1}$ soil for atrazine, and 0.050 $\mu\text{g kg}^{-1}$ for DEA and DIA. While the sensitivity of the GC exceeds that of the HPLC, the upper limit of detection of the GC is less than that of the HPLC. Average recoveries from sample spikes were 91% for carbofuran, 90% for atrazine, 88% for DEA, and 38% for DIA. It was not clear why the recovery rate for DIA was so low.

DISSIPATION RATES

The pesticide dissipation process, including volatilization, degradation, and transformation, is a function of temperature, soil-water, pH, carbon, clay, oxygen, nutrients, microbial population, acclimation, and concentration (Valentine and Schnoor, 1986). While the dissipation is a function of many parameters, the assumption is frequently made that it follows a first-order decay relationship:

$$\frac{dC}{dt} = -kC \quad (1)$$

where

C = concentration of pesticide in the soil (mass chemical/mass soil)

k = soil dissipation rate constant (day^{-1})

t = elapsed time since pesticide application (days)

Table 1. Application dates, application rates, irrigation applied immediately after pesticide application, annual precipitation, and annual irrigation for the three study years

| Year | Application Date | Atrazine Application Rate (kg ha^{-1}) | Carbofuran Application Rate (kg ha^{-1}) | Irrigation Application after immediately (cm) | Annual Precipitation (cm) | Annual Irrigation (cm) |
|------|------------------|---|---|---|---------------------------|------------------------|
| | | | | | | |
| 1993 | May 4 | 2.4 | 2.2 | 0.7 | 149 | 39 |
| 1994 | March 22 | 2.2 | 2.2 | 0.7 | 196 | 27 |
| 1995 | March 21 | 2.8 | 2.8 | 5.2 | 93 | 41 |

Integrating and defining C_0 as the concentration at application ($t = 0$) yields:

$$\frac{C}{C_0} = e^{-kt} \quad (2)$$

For the case where the decay is first order, plotting the logarithm of the concentration ratio against time will result in a straight line which when forced through zero has a slope equal to k (Hurlle and Walker, 1980). The equation can be used to determine the soil dissipation half life, $t_{1/2}$ (days), the time required for the compound to dissipate to half its concentration at $t = 0$.

$$t_{1/2} = \frac{-\ln(0.5)}{k} \quad (3)$$

RESULTS

SOIL CHARACTERIZATION

The two soils identified in the plot were a Pine Flat loamy sand (coarse-loamy, siliceous, thermic *Typic Paleudult*) and a Troup loamy sand (loamy, siliceous, thermic *Grossarenic Kandiudult*) (fig. 1). The Troup soil occupied approximately 84% of the plot area. The Pine Flat soil in the southeast corner of the plot contained a well developed argillic horizon between 50 and 250 cm which contains up to 28% clay (Bosch and West, 1998). The argillic horizon in the Troup soil occurs at greater depth (> 100 cm), and typically has less clay (~15%) and a more rapid saturated hydraulic conductivity throughout (Bosch and West, 1998).

While differences in soil characteristics exist across the plot, these differences have been discussed extensively in other studies (Bosch and West, 1998; Shaw et al., 1999) and were not the focus of this work. Average soil characteristics determined from core samples collected at each of the eight sites are shown in table 2. The surface soil at the site is high in sand content, with a high bulk density. These soils are low in organic carbon, and are slightly acid (pH around 5.0 soil:H₂O 1:1). The hydraulic conductivities of the surface soils are very high but decrease within the argillic horizons (table 2).

CLIMATIC CONDITIONS

Precipitation and irrigation patterns for 1993, 1994, and 1995 observed at the site were examined (fig. 2). The average annual precipitation for the site is 124 cm. Total precipitation and irrigation for 1993, 1994, and 1995 exceeded this average (table 1). The precipitation patterns in each of these years in the first 90 days of the year (January through March) were near normal, except in 1993 when the March precipitation was above normal. Precipitation and irrigation totals received on the plot in the critical period from April to June exceeded normal precipitation in each year. Temperature data collected at the University of Georgia Plains Experiment Station indicated air temperatures were fairly consistent with long term records. Average monthly maximum air temperatures range from a high of 33°C in July to a low of 14°C, while average monthly minimum air temperatures range from a high of 21°C in July to a low of 2°C in January.

SURFACE RUNOFF

In the three years of observation at the site, surface runoff only occurred twice. The first occurrence was on 5 and 6 July 1994, when 57 cm of rainfall was received over a five day period, causing 0.1 cm of runoff on 5 July and 7 cm on July 6. The second observed runoff was on 6 January 1995, when 2.6 cm of rainfall was received which generated a trace of runoff. During the 1994 runoff event the automatic runoff sampler was not working and no samples were collected. However, since this was quite late after pesticide application (105 days after) the amount of pesticide moving with this runoff was not expected to be large. During the 1995 runoff event the runoff depth was too low to trip sample collection.

METHODS COMPARISON

Because both HPLC and GC methods were used, a comparison between the results using the two instruments was made. In general, the values were within an order of magnitude (fig. 3). In the case of atrazine there were a group of eight points where both results exceed 8000 µg kg⁻¹, but the GC results were consistently greater than the HPLC results (fig. 3a). The HPLC results are expected to exceed the GC results at higher detection limits because the upper limit of detection is greater for the HPLC than for the GC. All of the measurements in this group of eight points were from samples collected one day after application in 1995 when the atrazine levels were

Table 2. Average soil characteristics for the study plot determined from core samples collected at each of the eight sites

| Depth Interval (cm) | Clay Fraction (%) | Sand Fraction (%) | Organic Carbon (%) | Bulk Density (gm/cm ³) | Saturated Moisture Content (cm ³ /cm ³) | Residual Moisture Content* (cm ³ /cm ³) | Saturated Hydraulic Conductivity (cm h ⁻¹) |
|---------------------|-------------------|-------------------|--------------------|------------------------------------|--|--|--|
| 0 - 1 | 5 | 89 | 0.51 | 1.40 | 0.27 | 0.06 | 34 |
| 0 - 12.5 | 4 | 87 | 0.40 | 1.60 | 0.27 | 0.06 | 33 |
| 12.5 - 25 | 5 | 87 | 0.40 | 1.60 | 0.26 | 0.06 | 26 |
| 25 - 37.5 | 5 | 84 | 0.20 | 1.65 | 0.22 | 0.06 | 25 |
| 37.5 - 50 | 6 | 84 | 0.10 | 1.65 | 0.22 | 0.06 | 21 |
| 50 - 75 | 6 | 83 | 0.08 | 1.65 | 0.23 | 0.06 | 14 |
| 75 - 100 | 6 | 82 | 0.05 | 1.70 | 0.22 | 0.07 | 14 |
| 100 - 150 | 12 | 82 | 0.04 | 1.70 | 0.21 | 0.07 | 15 |
| 150 - 200 | 15 | 75 | 0.05 | 1.70 | 0.22 | 0.07 | 11 |
| 200 - 250 | 14 | 76 | 0.05 | 1.70 | 0.22 | 0.07 | 26 |

* Moisture content at 15 bar pressure.

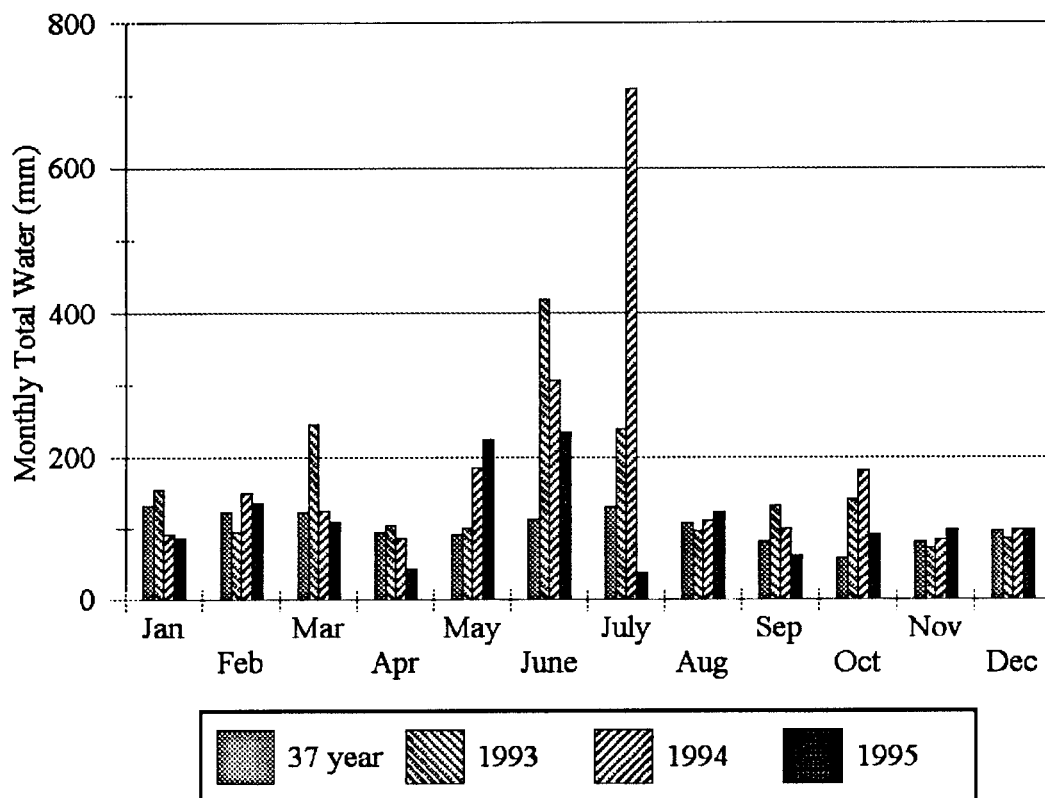


Figure 2—Total plot water, precipitation, and irrigation patterns for 1993, 1994, and 1995, and the 37 year average monthly precipitation for the area from 1959 to 1995.

extremely high. These samples were diluted prior to analysis on the GC. It is possible that with dilution, the GC results were more accurate because of the better accuracy of the instrument. Considerable variability was also observed between the carbofuran and the DEA data determined from the two analytical techniques. While trends were similar, neither technique was consistently higher or lower than the other.

For both analytical techniques measured values for spiked samples agreed well with actual concentrations. For the measurements presented here, both HPLC and GC data were used. Judgements were made based upon the expected accuracy of the results and what was believed to be the more accurate results used.

MEAN PESTICIDE BEHAVIOR

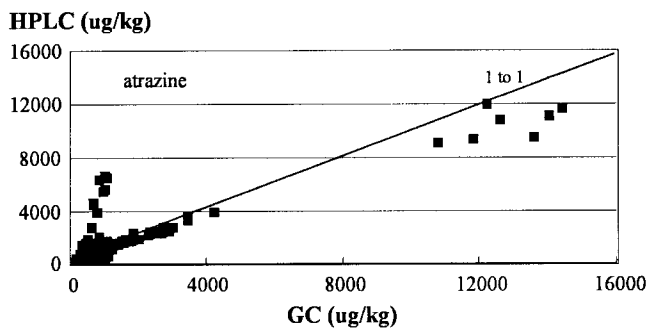
While samples were collected at each of the eight sites, only mean pesticide behaviors over the entire plot were examined for this analysis. Background concentrations of the compounds were measured using the soil samples collected in 1993 prior to the first pesticide application and found to be below the detection limits of the analytical techniques. Mean concentrations of atrazine, carbofuran, and DEA observed in each of the three years and DIA in 1994 along with the standard deviations of these samples with depth were calculated (tables 3 to 6). Atrazine was observed at the greatest concentrations in each of the three years and was more persistent in the soil than carbofuran. The greatest concentrations of both compounds were observed in 1995, the year with the greatest application rate.

In 1993 and 1994 approximately 0.7 cm of irrigation were applied immediately after chemical application. In 1995, 0.6 cm of irrigation was applied after application followed by 1.8 cm one day after application (following the soil sampling) and 2.8 cm on the second day after application. Despite the irrigations following application, the greatest concentrations of atrazine and carbofuran were found in the top 1 cm.

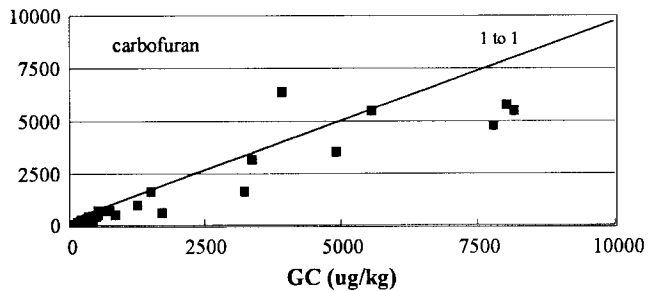
Dissipation occurred rapidly in the first 44 days after pesticide application each year. The greatest decrease in atrazine concentration was observed in 1995 when the average concentration in the surface sample decreased from $13\,200\ \mu\text{g kg}^{-1}$ 1 day after application to $2800\ \mu\text{g kg}^{-1}$ three days after. The initial losses of carbofuran were greater than the initial losses of atrazine. Carbofuran concentrations in the soil samples collected one day after application were considerably less than the atrazine concentrations, despite similar application rates. Carbofuran dissipated more rapidly than did atrazine and did not transport as deep in the profile.

The majority of the pesticides remained in the sampled depth throughout the first 44 days after pesticide application. However, elevated concentrations of the compounds in the bottom sample depths indicate some of the parent compound could have been transported below the sampled profile (tables 3 and 4). The greatest concentrations were consistently observed in the top 12.5 cm of the profile and there did not appear to be a clear movement of a plume of the parent compound.

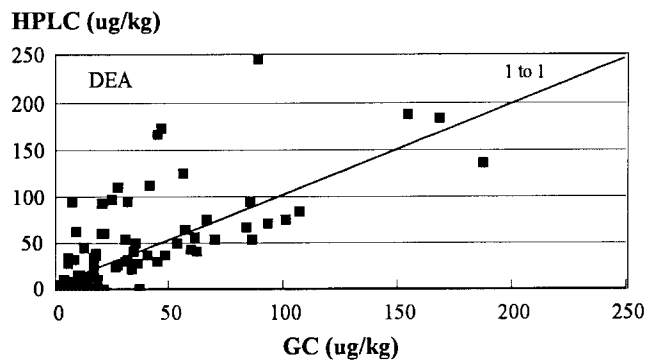
As expected, DEA and DIA concentrations fluctuated with time. Initial concentrations of DEA were quite high at



(a)



(b)



(c)

Figure 3—Comparison of data obtained through HPLC and GC analysis for atrazine, carbofuran, and deethylatrazine (DEA).

one day after pesticide application in 1993 and again in 1995, indicating that either there was some DEA present with the parent compound at application or there was rapid transformation from atrazine to DEA. The concentrations of DIA and DEA in the applied atrazine formulation were not measured. However, studies which have looked at the concentrations of DIA and DEA in the applied atrazine have not found detectable levels within the parent formulation (Adams and Thurman, 1991). Rapid transformation of atrazine into DEA has been attributed to deethylation by soil microorganisms (Adams and Thurman, 1991).

In 1993, there did not appear to be an increase in DEA later in the growing season while in 1994 and 1995 an increase was observed from 7 to 14 days after application. The DIA concentrations were not as large as DEA concentrations nor were they as elevated at one day after application. DIA is more mobile than DEA

(Jayachandran et al., 1994) which could lead to more rapid leaching out of the sampled profile. However, profile data collected for this study indicate that only low levels of DIA were being transported and formed at the bottom of the soil profile (table 6). The DIA concentrations also increased up to 14 days after application in 1994 and decreased thereafter. Because our recovery rates on spiked DIA samples were just 38%, it is likely that we did not recover all of the DIA in the sample. Thus, the DIA concentrations which we observed were likely less than actual DIA concentrations in the soil profile.

MASS BALANCE AND DISSIPATION RATES

Average soil concentrations and bulk densities were used to calculate mass balances for atrazine and carbofuran, and accumulated mass of DEA and DIA (table 7). Dates greater than 44 days after application included samples down to the water table. Overall, the atrazine and carbofuran mass balance in the first sample, one day after application, was quite good. Either the sample exceeded 100% of the applied compound or was slightly less. However, in 1993 only 48% of the applied carbofuran was measured in the samples collected one day after application, suggesting greater dissipation during this year. In 1993, planting and application occurred later than normal (5 May). Because it was later in the growing season, air and soil temperatures were greater, which may have led to increased dissipation during 1993. However, we did not observe this same increase in dissipation in 1993 for atrazine.

It is also not clear why the percent recovery for the first sample collected exceeded 100% for some years. Some deviation from 100% is expected due to application and soil variability. While application variability was not quantified in this study, previous measurements using the same equipment indicate fairly uniform distributions. Coefficients of variability ranged from 13 to 45% for the pesticide data for the 1 cm sample 1 day after application. Values in excess of 100% could also have resulted due to the variability in the soil concentrations as well.

The 5.2 cm of irrigation in the first three days after application in 1995 may have led to increased recoveries and slower dissipation rates during that year by transporting the chemicals below the more biologically active surface layer. While atrazine appeared to degrade less rapidly in 1995, Carbofuran degraded at approximately the same rate as in 1993 and 1994. Application methods and chemical formulations were the same for all three years. However, since application dates and climatic influences varied each year different dissipation rates can be expected.

A linear regression with a forced zero intercept was fit to the observed dissipation data and dissipation rates and soil half lives calculated for the parent compounds for each individual year as well as for the aggregated three years of data (table 8). Soil half lives for atrazine ranged from 13 days in 1993 to 47 days in 1994. When all three years of data were used the pesticide dissipation constant calculated for atrazine was 0.018 with a half life of 38 days. Soil half lives for carbofuran ranged from a low of 9 days in 1993 to a high of 23 days in 1994. Using all three years of data the dissipation constant calculated for carbofuran was 0.035 with a soil half life of 20 days.

Table 3. Observed mean concentrations and standard deviations (stds) for atrazine in the soil profile for the first 44 days after pesticide application (DAPA) in 1993, 1994, and 1995

| Top of Sample Depth (cm) | Bottom of Sample Depth (cm) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) |
|--------------------------|-----------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|
| 1993 Concentrations | | 1 DAPA | | 3 DAPA | | 8 DAPA | | 15 DAPA | | 29 DAPA | | 43 DAPA | |
| 0 | 1 | 6826 | 1387 | 6432 | 1292 | 3097 | 437 | 1648 | 344 | 429 | 89 | 53 | 51 |
| 0 | 12.5 | 987 | 222 | 642 | 395 | 372 | 78 | 320 | 53 | 109 | 70 | 12 | 11 |
| 12.5 | 25 | 72 | 34 | 321 | 243 | 149 | 75 | 46 | 24 | 19 | 11 | 12 | 21 |
| 25 | 50 | 45 | 31 | 40 | 17 | 80 | 93 | 5 | 9 | 4 | 9 | 1 | 3 |
| 50 | 75 | 25 | 18 | 37 | 42 | 10 | 11 | 1 | 3 | bd* | 0 | 3 | 3 |
| 75 | 100 | 34 | 31 | 26 | 8 | 7 | 8 | 10 | 28 | bd | 0 | 2 | 5 |
| 100 | 150 | ns† | ns | ns | ns | ns | ns | 4 | 9 | 2 | 3 | 1 | 4 |
| 150 | 200 | ns | ns | ns | ns | ns | ns | ns | ns | bd | 0 | 0 | 1 |
| 200 | 250 | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | 0 | 0 |
| 1994 Concentrations | | 1 DAPA | | 3 DAPA | | 7 DAPA | | 14 DAPA | | 28 DAPA | | 44 DAPA | |
| 0 | 1 | 5503 | 1036 | 1570 | 682 | 647 | 111 | 711 | 286 | 246 | 45 | 81 | 26 |
| 0 | 12.5 | 886 | 375 | 945 | 275 | 603 | 80 | 711 | 261 | 254 | 45 | 84 | 48 |
| 12.5 | 25 | 173 | 81 | 90 | 140 | 101 | 64 | 100 | 72 | 81 | 56 | 30 | 24 |
| 25 | 50 | 45 | 27 | 7 | 2 | 14 | 7 | 8 | 4 | 10 | 5 | 10 | 13 |
| 50 | 75 | 24 | 34 | 5 | 0 | 8 | 4 | 6 | 3 | 7 | 2 | 2 | 2 |
| 75 | 100 | 10 | 5 | 5 | 1 | 8 | 3 | 5 | 2 | 5 | 1 | 1 | 1 |
| 100 | 150 | ns | ns | ns | ns | ns | ns | 7 | 3 | 7 | 3 | 0 | 1 |
| 150 | 200 | ns | ns | ns | ns | ns | ns | ns | ns | 5 | 1 | 0 | 1 |
| 200 | 250 | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | 1 | 4 |
| 1995 Concentrations | | 1 DAPA | | 3 DAPA | | 7 DAPA | | 14 DAPA | | 28 DAPA | | 44 DAPA | |
| 0 | 1 | 13 215 | 1706 | 2804 | 956 | 1780 | 858 | 733 | 81 | 349 | 104 | 138 | 112 |
| 0 | 12.5 | 1527 | 778 | 1259 | 554 | 1045 | 356 | 518 | 88 | 120 | 83 | 54 | 39 |
| 12.5 | 25 | 314 | 256 | 382 | 239 | 349 | 160 | 204 | 123 | 47 | 32 | 25 | 22 |
| 25 | 50 | 49 | 29 | 23 | 9 | 19 | 19 | 9 | 6 | 12 | 19 | 3 | 3 |
| 50 | 75 | 21 | 25 | 12 | 3 | 11 | 11 | 4 | 3 | 2 | 2 | 1 | 0 |
| 75 | 100 | ns | ns | 8 | 5 | 7 | 5 | 4 | 3 | 1 | 1 | 0 | 0 |
| 100 | 150 | ns | ns | 7 | 3 | 5 | 4 | 2 | 1 | 1 | 1 | 1 | 1 |
| 150 | 200 | ns | ns | ns | ns | ns | ns | ns | ns | 1 | 1 | 1 | 0 |
| 200 | 250 | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | 1 | 1 |

* Below detection.

† No sample.

The first-order decay relationship fit the overall behavior of the data fairly well for the period soon after pesticide application, but failed to represent the portion of the decay curve from 20 to 150 days (figs. 4 and 5). The correlation coefficient, r , between the observed and predicted values of the percent of the applied pesticide remaining was 0.86 for atrazine and 0.71 for carbofuran. The rate of dissipation decreases rapidly after a rapid initial decay. Most field studies typically examine the first 60 days after pesticide application. In these cases, the first order rate equation appears to fit fairly well (Topp et al., 1994; Wauchope et al., 1991; Weed et al., 1998). However, in field studies which have looked at longer time frames, a two-stage dissipation has been observed (Workman et al., 1998; Workman et al., 1995; Smith et al., 1978). This two-stage dissipation has been attributed to a movement of the chemical from sites in the soil where the degradation process is rapid to less exposed sites in the soil (Hill and Schaalje, 1985; Wauchope et al., 1991). Often, when used for modeling, a two-stage model provides a better fit to observed data (Truman et al., 1998; Ma et al., 1995).

Using the data collected in this study, a two-stage model was developed with an initial period of rapid dissipation and a second for the remaining portion of the curve (figs. 4 and 5). A dissipation rate was calculated through regression with a forced zero intercept for the observed data up to 44 days after application (table 8). A

second dissipation rate was calculated through regression with a nonzero intercept for the observed data 44 days after application and greater. The dissipation relationships evaluated through this method were;

$$C = C_0 e^{(-0.059t)} \quad t \leq 44 \quad (4)$$

$$C = C_0 e^{(-0.006t - 2.332)} \quad t > 44 \quad (5)$$

for atrazine, and;

$$C = C_0 e^{(-0.110t)} \quad t \leq 44 \quad (6)$$

$$C = C_0 e^{(-0.018t - 4.048)} \quad t > 44 \quad (7)$$

for carbofuran.

The correlation coefficient, r , between the observed and predicted values using the two-stage model was 0.96 for atrazine and 0.78 for carbofuran. A 77% reduction in the sum of squares of the difference between the observed and predicted values was obtained by using the two-stage model for atrazine and a 50% reduction was obtained for the carbofuran model. These models would be more appropriate for modeling the decay rates of the compounds. Since the most critical period is in the first 40 days after pesticide application, it is important to fit this period as accurately as possible.

Table 4. Observed mean concentrations and standard deviations (stds) for carbofuran in the soil profile for the first 44 days after pesticide application (DAPA) in 1993, 1994, and 1995

| Top of Sample Depth (cm) | Bottom of Sample Depth (cm) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) |
|--------------------------|-----------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|
| 1993 Concentrations | | 1 DAPA | | 3 DAPA | | 8 DAPA | | 15 DAPA | | 29 DAPA | | 43 DAPA | |
| 0 | 1 | 2416 | 1076 | 2415 | 1293 | 2145 | 379 | 1404 | 774 | 638 | 264 | 18 | 20 |
| 0 | 12.5 | 521 | 337 | 270 | 266 | 172 | 121 | 358 | 129 | 221 | 111 | 15 | 15 |
| 12.5 | 25 | 12 | 17 | 81 | 122 | 48 | 55 | 42 | 47 | 35 | 36 | 23 | 19 |
| 25 | 50 | 6 | 9 | 4 | 8 | 7 | 17 | 5 | 7 | 0 | 1 | 17 | 13 |
| 50 | 75 | 2 | 2 | 5 | 11 | 7 | 8 | 1 | 3 | bd* | 0 | 11 | 15 |
| 75 | 100 | 1 | 4 | bd | 0 | 3 | 6 | 17 | 24 | 3 | 9 | 4 | 7 |
| 100 | 150 | ns† | ns | ns | ns | ns | ns | 20 | 22 | 1 | 3 | 15 | 19 |
| 150 | 200 | ns | ns | ns | ns | ns | ns | ns | ns | bd | 0 | 14 | 22 |
| 200 | 250 | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | 4 | 7 |
| 1994 Concentrations | | 1 DAPA | | 3 DAPA | | 7 DAPA | | 14 DAPA | | 28 DAPA | | 44 DAPA | |
| 0 | 1 | 3467 | 609 | 437 | 230 | 132 | 44 | 43 | 46 | 20 | 4 | bd | 0 |
| 0 | 12.5 | 944 | 453 | 566 | 245 | 179 | 117 | 23 | 21 | 17 | 5 | bd | 0 |
| 12.5 | 25 | 45 | 54 | 103 | 119 | 131 | 61 | 12 | 14 | 7 | 6 | bd | 0 |
| 25 | 50 | 5 | 10 | ns | ns | bd | 0 | 4 | 11 | 4 | 9 | bd | 0 |
| 50 | 75 | 7 | 20 | ns | ns | bd | 0 | bd | 0 | 2 | 6 | bd | 0 |
| 75 | 100 | bd | 0 | ns | ns | bd | 0 | bd | 0 | bd | 0 | bd | 0 |
| 100 | 150 | ns | ns | ns | ns | ns | ns | bd | 0 | bd | 0 | bd | 0 |
| 150 | 200 | ns | ns | ns | ns | ns | ns | ns | ns | bd | 0 | bd | 0 |
| 200 | 250 | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | bd | 0 |
| 1995 Concentrations | | 1 DAPA | | 3 DAPA | | 7 DAPA | | 14 DAPA | | 28 DAPA | | 44 DAPA | |
| 0 | 1 | 5397 | 2454 | 353 | 225 | 262 | 111 | 210 | 68 | 55 | 50 | 23 | 21 |
| 0 | 12.5 | 1107 | 962 | 188 | 126 | 144 | 49 | 66 | 22 | 5 | 11 | 21 | 18 |
| 12.5 | 25 | 103 | 123 | 27 | 20 | 28 | 10 | 13 | 14 | bd | 0 | 22 | 15 |
| 25 | 50 | 8 | 7 | bd | 0 | 2 | 5 | bd | 0 | bd | 0 | 6 | 8 |
| 50 | 75 | 3 | 4 | bd | 0 | 2 | 6 | bd | 0 | bd | 0 | 17 | 14 |
| 75 | 100 | ns | ns | bd | 0 | bd | 0 | bd | 0 | bd | 0 | 18 | 21 |
| 100 | 150 | ns | ns | bd | 0 | bd | 0 | bd | 0 | 0 | 1 | 19 | 17 |
| 150 | 200 | ns | ns | ns | ns | ns | ns | ns | ns | bd | 0 | 6 | 8 |
| 200 | 250 | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | 11 | 12 |

* Below detection.

† No sample.

DISCUSSION

Rapid transport of the pesticides down to 100 cm was observed in the first day after application (tables 3 to 6). Downward transport of the compounds appeared to slow after the first day. However, in 1993 we did not measure below 100 cm until 15 days after application and not until 14 days after in 1994. Such rapid downward transport one day after application was not expected. It may have been due to the irrigation water applied after application, aided by macropore flow. However there was no other evidence of macropores in this soil and the soil is very poorly structured due to the high sand and low clay contents. Because of this we did not measure below 100 cm during the first sampling. By the time samples were collected below 100 cm sufficient degradation and dilution had taken place to reduce the concentrations. The compounds may have moved below 100 cm between the time of application and the 15 day sampling.

The soil had a reduced hydraulic conductivity below 50 cm (table 2). This may have slowed the chemical transport once it reached the area from 50 to 100 cm. In addition, the clay content increased dramatically below 100 cm which may have increased adsorption. These factors may have also contributed to the lower concentrations observed below 100 cm.

As illustrated by the dissipation coefficients, atrazine and carbofuran degraded rapidly (figs. 4 and 5). On the

average, by 30 days after application 83% of the atrazine and 96% of the carbofuran had degraded. By 44 days after application, virtually all of the pesticides in the top 250 cm of the soil degraded.

The soil based dissipation half lives observed in this study were within the range of those previously reported in the literature. These half lives reflect all dissipation processes including volatilization, decay, and transport. The soil based half life reported by Hornsby et al. (1996) for atrazine is 60 days while for carbofuran it is 50 days. Lab studies by Topp et al. (1994) reported half lives from 15 to 54 days for atrazine, while lab studies using soils from Hawaii by Green et al. (1993) yielded half lives varying from 8 to 81 days. Field studies conducted by Heatwole et al. (1997) resulted in half lives varying from 116 days to 215 days for atrazine. Field studies conducted by Workman et al. (1995) in Ohio found half lives for atrazine from 31 to 54 days. This illustrates the wide variability of dissipation rates observed in various soils. The dissipation rates calculated in this study exhibited less overall variability than many of these other studies.

A DEA to atrazine ratio (DAR) has been suggested as an indicator of residence time in soil during atrazine transport (Jayachandran et al., 1994) and as an indicator of soil-mediated transport of atrazine to an aquifer (Adams and Thurman, 1991). Prolonged residence time in soil should result in larger DAR values. It is believed that in the case

Table 5. Observed mean concentrations and standard deviations (stds) for deethylatrazine in the soil profile for the first 44 days after pesticide application (DAPA) in 1993, 1994, and 1995

| Top of Sample Depth (cm) | Bottom of Sample Depth (cm) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) |
|--------------------------|-----------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|
| 1993 Concentrations | | 1 DAPA | | 3 DAPA | | 8 DAPA | | 15 DAPA | | 29 DAPA | | 43 DAPA | |
| 0 | 1 | 92 | 43 | 89 | 66 | 36 | 18 | 17 | 13 | 4 | 7 | 1 | 2 |
| 0 | 12.5 | 17 | 20 | 7 | 6 | 3 | 5 | 8 | 16 | 25 | 18 | 26 | 16 |
| 12.5 | 25 | 5 | 7 | 3 | 3 | 0 | 1 | 1 | 4 | 40 | 43 | 52 | 56 |
| 25 | 50 | 6 | 13 | 1 | 2 | bd* | 0 | bd | 0 | bd | 0 | 25 | 50 |
| 50 | 75 | 2 | 3 | 1 | 3 | bd | 0 | bd | 0 | bd | 0 | bd | 0 |
| 75 | 100 | 2 | 4 | 0 | 0 | bd | 0 | bd | 0 | bd | 0 | bd | 0 |
| 100 | 150 | ns† | ns | ns | ns | ns | ns | bd | 0 | bd | 0 | 0 | 1 |
| 150 | 200 | ns | ns | ns | ns | ns | ns | ns | ns | bd | 0 | 0 | 0 |
| 200 | 250 | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | 0 | 0 |
| 1994 Concentrations | | 1 DAPA | | 3 DAPA | | 7 DAPA | | 14 DAPA | | 28 DAPA | | 44 DAPA | |
| 0 | 1 | 17 | 8 | 9 | 2 | 25 | 6 | 44 | 38 | 24 | 13 | 12 | 13 |
| 0 | 12.5 | 8 | 2 | 7 | 2 | 27 | 6 | 43 | 20 | 33 | 10 | 12 | 10 |
| 12.5 | 25 | 4 | 3 | 3 | 4 | 7 | 8 | 10 | 10 | 15 | 7 | 10 | 10 |
| 25 | 50 | 2 | 2 | 1 | 2 | 2 | 4 | bd | 0 | 4 | 3 | 3 | 5 |
| 50 | 75 | 0 | 1 | 2 | 2 | 1 | 2 | bd | 0 | 1 | 2 | bd | 0 |
| 75 | 100 | 1 | 3 | 2 | 3 | 1 | 3 | bd | 0 | 1 | 2 | bd | 0 |
| 100 | 150 | ns | ns | ns | ns | ns | ns | bd | 0 | 1 | 2 | bd | 0 |
| 150 | 200 | ns | ns | ns | ns | ns | ns | ns | ns | 1 | 2 | bd | 0 |
| 200 | 250 | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | bd | 0 |
| 1995 Concentrations | | 1 DAPA | | 3 DAPA | | 7 DAPA | | 14 DAPA | | 28 DAPA | | 44 DAPA | |
| 0 | 1 | 102 | 38 | 31 | 13 | 82 | 51 | 25 | 14 | 14 | 10 | 21 | 12 |
| 0 | 12.5 | 18 | 7 | 14 | 6 | 45 | 14 | 25 | 9 | 16 | 12 | 21 | 6 |
| 12.5 | 25 | 3 | 2 | 7 | 3 | 9 | 6 | 4 | 4 | 4 | 4 | 16 | 5 |
| 25 | 50 | 0 | 0 | 0 | 0 | bd | 0 | bd | 0 | bd | 0 | 11 | 6 |
| 50 | 75 | 0 | 0 | 0 | 0 | bd | 0 | bd | 0 | bd | 0 | 13 | 9 |
| 75 | 100 | ns | ns | bd | 0 | bd | 0 | bd | 0 | bd | 0 | 14 | 6 |
| 100 | 150 | ns | ns | bd | 0 | bd | 0 | bd | 0 | bd | 0 | 13 | 8 |
| 150 | 200 | ns | ns | ns | ns | ns | ns | ns | ns | bd | 0 | 15 | 14 |
| 200 | 250 | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | 13 | 8 |

* Below detection.

† No sample.

Table 6. Observed mean concentrations and standard deviations (stds) for deisopropylatrazine in the soil profile for the first 44 days after pesticide application (DAPA) in 1994

| Top of Sample Depth (cm) | Bottom of Sample Depth (cm) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) | Mean ($\mu\text{g kg}^{-1}$) | Stds. ($\mu\text{g kg}^{-1}$) |
|--------------------------|-----------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|
| 1994 Concentrations | | 1 DAPA | | 3 DAPA | | 7 DAPA | | 14 DAPA | | 28 DAPA | | 44 DAPA | |
| 0 | 1 | 3 | 3 | 2 | 2 | 10 | 5 | 11 | 5 | 10 | 3 | 1 | 1 |
| 0 | 12.5 | 1 | 2 | 1 | 2 | 11 | 5 | 11 | 5 | 11 | 2 | bd* | 0 |
| 12.5 | 25 | 0 | 1 | 1 | 2 | 2 | 4 | 1 | 4 | 4 | 3 | bd | 0 |
| 25 | 50 | 0 | 1 | 1 | 2 | bd | 0 | bd | 0 | bd | 0 | bd | 0 |
| 50 | 75 | 1 | 2 | 1 | 2 | bd | 0 | bd | 0 | bd | 0 | bd | 0 |
| 75 | 100 | 0 | 1 | 0 | 1 | bd | 0 | bd | 0 | bd | 0 | bd | 0 |
| 100 | 150 | ns† | ns | ns | ns | ns | ns | bd | 0 | bd | 0 | bd | 0 |
| 150 | 200 | ns | ns | ns | ns | ns | ns | ns | ns | bd | 0 | bd | 0 |
| 200 | 250 | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | bd | 0 |

* Below detection.

† No sample.

of macropore flow, a low DAR would be indicative of rapid transport through the root zone. Ratios of the metabolite mass to parent mass ranged from 0 to 4.5 for DEA and from 0 to 1 for DIA. While the trend was for an increased ratio as time since application increased, there was considerable variability.

It was interesting to note that the dissipation rates for the two parent compounds followed similar trends each year. The shortest half life for both compounds was

observed in 1993 while the longest was observed in 1994. The more rapid dissipation observed in 1993 could have been due to the higher temperatures at application, since application did not occur until 4 May. Soil-water conditions were similar each year due to irrigation.

Table 7. Mass balances for atrazine and carbofuran, and accumulated mass of deethylatrazine (DEA) and deisopropylatrazine (DIA) in the sampled soil profile

| Date | Days After Pesticide Application | Atrazine Mass (kg) | Atrazine % of Yearly Application | Carbofuran Mass (kg) | Carbofuran % of Yearly Application | DIA Mass (kg) | DEA Mass (kg) |
|----------|----------------------------------|--------------------|----------------------------------|----------------------|------------------------------------|---------------|---------------|
| 5/5/93 | 1 | 2.47 | 103 | 1.06 | 48 | nm* | 0.08 |
| 5/7/93 | 3 | 2.31 | 96 | 0.72 | 33 | nm | 0.03 |
| 5/12/93 | 8 | 1.41 | 59 | 0.50 | 23 | nm | 0.01 |
| 5/19/93 | 15 | 0.81 | 34 | 1.04 | 47 | nm | 0.02 |
| 6/2/93 | 29 | 0.28 | 12 | 0.52 | 24 | nm | 0.13 |
| 6/16/93 | 43 | 0.09 | 4 | 0.48 | 22 | nm | 0.26 |
| 8/12/93 | 100 | 0.02 | 1 | 0.00 | 0 | nm | 0.00 |
| 3/23/94 | 1 | 2.38 | 108 | 1.96 | 89 | 0.01 | 0.04 |
| 3/25/94 | 3 | 2.07 | 94 | 1.30 | 59 | 0.01 | 0.04 |
| 3/29/94 | 7 | 1.49 | 68 | 0.61 | 28 | 0.03 | 0.08 |
| 4/5/94 | 14 | 1.71 | 78 | 0.09 | 4 | 0.02 | 0.10 |
| 4/19/94 | 28 | 0.84 | 38 | 0.07 | 3 | 0.03 | 0.14 |
| 5/5/94 | 44 | 0.29 | 13 | 0.00 | 0 | 0.00 | 0.06 |
| 9/14/94 | 176 | 0.15 | 7 | 0.00 | 0 | 0.00 | 0.00 |
| 3/14/95 | 357 | 0.01 | 1 | 0.00 | 0 | 0.01 | md† |
| 3/22/95 | 1 | 3.87 | 138 | 2.39 | 85 | nm | 0.04 |
| 3/24/95 | 3 | 3.43 | 123 | 0.42 | 15 | nm | 0.04 |
| 3/28/95 | 7 | 2.91 | 104 | 0.35 | 12 | nm | 0.11 |
| 4/4/95 | 14 | 1.50 | 54 | 0.15 | 5 | nm | 0.06 |
| 4/18/95 | 28 | 0.41 | 15 | 0.01 | 0 | nm | 0.04 |
| 5/4/95 | 44 | 0.19 | 7 | 0.55 | 20 | nm | 0.56 |
| 10/31/95 | 224 | 0.06 | 2 | 0.00 | 0 | nm | 0.29 |

* Not measured.

† Missing data.

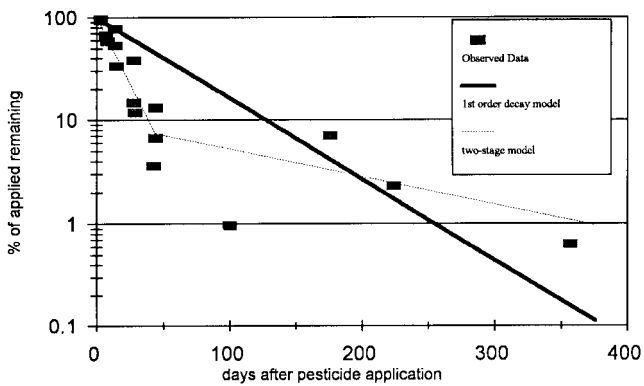


Figure 4—Observed and predicted atrazine remaining in the soil profile during the study period.

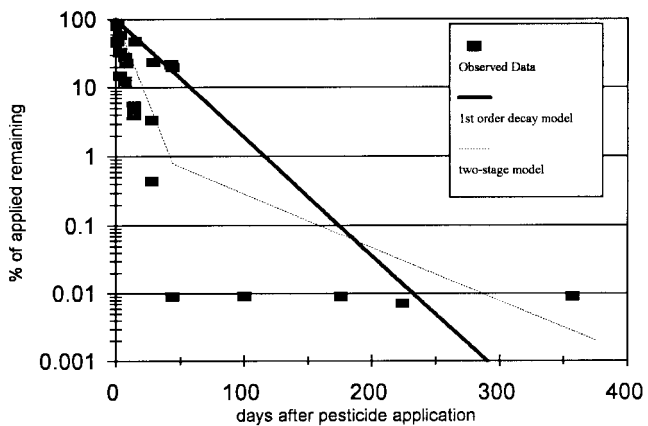


Figure 5—Observed and predicted carbofuran remaining in the soil profile during the study period.

Table 8. Dissipation rates and soil half lives for atrazine and carbofuran for each individual year and for the aggregated three years of data

| Time Frame | Soil Degradation Constant (day ⁻¹) | | Soil Half Life (days) | |
|--|--|------------|-----------------------|------------|
| | Atrazine | Carbofuran | Atrazine | Carbofuran |
| 1993 | 0.053 | 0.082 | 13.1 | 8.5 |
| 1994 | 0.015 | 0.034 | 46.7 | 20.3 |
| 1995 | 0.019 | 0.046 | 36.0 | 15.2 |
| All three years, all data | 0.018 | 0.040 | 38.4 | 17.5 |
| All three years, first 44 days after application | 0.059 | 0.110 | 11.7 | 6.3 |

CONCLUSIONS

Atrazine and carbofuran were found to dissipate rapidly within the sandy soils at the middle Georgia field site. Surface runoff was found to be insignificant relative to the overall hydrologic budget. A first-order decay model and a two-stage decay model were fit to the observed atrazine and carbofuran soil data. Atrazine was more persistent than was carbofuran with a half life roughly twice that for carbofuran. For the simple first-order decay model (eq. 3) a half life of 38 days was found for atrazine while a half life of 18 days was found for carbofuran. When a two-stage decay model was fit to the data, a soil half life of 12 days was found for atrazine for the first 44 days after application. A half life of six days fit the observed carbofuran data best for the first 44 days after application. The dissipation rate decreased rapidly after the first 44 days after application. For $t > 44$ days, the dissipation rate coefficient decreased from 0.059 to 0.006 (days⁻¹) for atrazine, while for carbofuran it decreased from 0.110 to 0.018 (days⁻¹). The two-stage model yielded a 77%

reduction in the sum of squares of the difference between the observed and predicted values for atrazine and a 50% reduction for carbofuran.

Observed levels of the atrazine metabolites DIA and DEA were highest in the top 1 cm of the soil. There appeared to be some movement or creation of the metabolites at lower depths in the profile later in the growing season, but not at large concentrations. Large concentrations of DEA and DIA were observed 1 day after application. This was followed by a decrease in DEA and DIA, and later by an increase around seven days after application. The later increases were likely due to transformation of the parent into the metabolite forms. No obvious trends with time were detected in the DAR. While DAR increased with increasing days after application, there was considerable variability.

Overall, the higher concentration levels of atrazine, atrazine metabolites, and carbofuran were limited to the top 25 cm of the profile and to the period from 1 to 30 days after application. Despite the sandy nature of the soils studied, the amount of the pesticides transported deeper in the soil profile was small. The high temperatures typical of the area and adequate soil-water conditions due to irrigation contributed to rapid decay of the parent compounds and metabolites. This reduces the risk of groundwater contamination due to matrix flow, but does not rule out transport due to preferential flow. These data and decay coefficients should be useful for chemical transport modeling. As models become more complex, the need for accurate transport measurements increases. Knowledge of soil micro-organisms, soil-water, and soil-temperature, are all required for a better model of this process. While half life lumps all dissipation processes, it does present a means of evaluating chemical decay and transport and a means of comparing chemicals.

ACKNOWLEDGMENTS. The authors wish to thank Dr. Joe Shaw and Dr. Don Wauchope for their review comments, and Ms. Luz Marti, Ms. Margie Whittle, and Ms. Sally Bellflower for their assistance with the chemical analysis. We also thank Mr. Shaw Fletcher, Mr. Ricky Fletcher, Mr. George Barfield, and Mr. Homer Allison for their assistance with sample collection and field work.

REFERENCES

- Adams, C. D., and E. M. Thurman. 1991. Formation and transport of deethylatrazine in the soil and vadose zone. *J. Environ. Qual.* 20(3): 540-547.
- Beck, B. F., L. Asmussen, and R. Leonard. 1985. Relationship of geology, physiography, agricultural land use, and ground-water quality in Southwest Georgia. *Ground Water* 23(5): 627-634.
- Belluck, D. A., S. L. Benjamin, and T. Dawson. 1991. Groundwater contamination by atrazine and its metabolites. In *Pesticide Transformation Products: Fate and Significance in the Environment*, eds. L. Somasundaram, and J. R. Coats, 254-273. ACS Symp. Ser. 459. Washington, D.C.: Am. Chem. Soc.
- Bosch, D. D., R. A. Leonard, C. C. Truman, L. T. West, and D. W. Hicks. 1997. Impacts of conventional agricultural practices on aquifer water quality: An overview of the Plains, Georgia water quality study. In *Proc. 1997 Georgia Water Resources Conference*, ed. K. Hatcher, 504-507. Athens, Ga.: University of Georgia.
- Bosch, D. D., and L. T. West. 1998. Hydraulic conductivity variability for two sandy soils. *Soil Sci. Soc. of Am. J.* 62(1): 90-98.
- Clark, W. Z., and A. C. Zisa. 1976. Physiographic map of Georgia. Georgia Geological Survey, Atlanta, Ga. Map SM-4, reprinted 1988, scale 1:2,000,000.
- Fermanich, K. J., W. L. Bland, B. Lowery, and M. McSweeney. 1996. Irrigation and tillage effects on atrazine and metabolite leaching from a sandy soil. *J. Environ. Qual.* 25(6): 1291-1299.
- Gaynor, J. D., D. C. MacTavish, and W. I. Findlay. 1995. Atrazine and metolachlor loss in surface and subsurface runoff from three tillage treatments in corn. *J. Environ. Qual.* 24(2): 246-256.
- Goodrich, J. A., B. W. Lykins Jr., and R. M. Clark. 1991. Drinking water from agriculturally contaminated groundwater. *J. Environ. Qual.* 20(4): 707-717.
- Green, R. E., R. C. Schneider, R. T. Gavenda, and C. J. Miles. 1993. Utility of sorption and degradation parameters from the literature for site-specific pesticide impact assessments. In *Sorption and Degradation of Pesticides and Organic Chemicals in Soil*, eds. D. M. Linn, T. H. Carski, M. L. Brusseau, and F. H. Chang. Madison, Wis.: SSSA.
- Heatwole, C. D., S. Zacharias, S. Mostaghimi, and T.A. Dillaha. 1997. Movement of field-applied atrazine, metolachlor, and bromide in a sandy loam soil. *Transactions of the ASAE* 40(5):1267-1276.
- Hill, B. D., and G. B. Schaalje. 1985. A two-compartment model for the dissipation of deltamethrin from soil. *J. Agric. Food Chem.* 33(3): 1001-1006.
- Hornsby, A.G., R. D. Wauchope, and A. E. Hermer. 1996. *Pesticide Properties in the Environment*. New York: Springer-Verlag.
- Hurle, K., and A. Walker. 1980. Persistence and its prediction. In *Interactions between Herbicides and the Soil*, ed. R. J. Hance. 83-122. London: Academic Press.
- Jayachandran, K., T. R. Steinheimer, L. Somasundaram, T. B. Moorman, R. S. Kanwar, and J. R. Coats. 1994. Occurrence of atrazine and degradates as contaminants of subsurface drainage and shallow groundwater. *J. Environ. Qual.* 23(2): 311-319.
- Klute, A. 1986. Water retention: Laboratory methods. In *Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods*, ed. A. Klute, 635-662. Madison, Wis.: Am. Soc. Agronomy.
- Klute, A., and C. Dirksen. 1986. Hydraulic conductivity and diffusivity: Laboratory methods. In *Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods*, ed. A. Klute, 687-734. Madison, Wis.: Am. Soc. of Agronomy.
- Leonard, R. A., G. W. Langdale, and W. G. Fleming. 1979. Herbicide runoff from upland Piedmont watersheds - Data and implications for modeling pesticide transport. *J. Environ. Qual.* 8(2): 223-229.
- Leonard, R. A., A. Shirmohammadi, A. W. Johnson, and L. R. Marti. 1988. Pesticide transport in shallow groundwater. *Transactions of the ASAE* 31(3): 776-788.
- Ma, Q. L., L. R. Ahuja, K. W. Rojas, V. F. Ferreira, and D. G. DeCoursey. 1995. Measured and RZWQM predicted atrazine dissipation and movement in a field soil. *Transactions of the ASAE* 38(2): 471-479.
- McFadden, S. S., and P. D. Perriello. 1983. Hydrogeology of the Clayton and Claiborne aquifers in Southwestern Georgia. Department of Natural Resources, Environmental Protection Division, Georgia Geologic Survey. Information Circular 55. Atlanta, Ga.
- Shaw, J. N., L. T. West, D. E. Radcliffe, and D. D. Bosch. 2000. Preferential flow and pedotransfer functions for transport properties in sandy kandiudults. *Soil Sci. Soc. of Am. J.* 64(2):670-678.
- Smith, C. N., R. A. Leonard, G. W. Langsdale, and G. W. Bailey. 1978. Transport of agricultural chemicals from small upland Piedmont watersheds. U.S. EPA Publication 600/3-78-056. Athens, Ga. U.S. Environ. Protection Agency.

- Topp, E., W. N. Smith, W. D. Reynolds, and S. U. Khan. 1994. Atrazine and metolachlor dissipation in soils incubated in undisturbed cores, repacked cores, and flasks. *J. Environ. Qual.* 23(4):693-700.
- Truman, C. C., R. A. Leonard, and F. M. Davis. 1998. GLEAMS-TC: A two compartment model for simulating temperature and soil water content effects on pesticide losses. *Soil Sci.* 163(5): 362-373.
- U.S. Environmental Protection Agency. 1990. Findings and results. In National survey of pesticides in drinking water wells: Phase I report. 51-88. USEPA Rep. 570/9-90-015. Washington, DC. GPO.
- Valentine, R. L., and J. L. Schnoor. 1986. Biotransformation. In *Vadose Zone Modeling of Organic Pollutants*, eds. S. C. Hern, and S. M. Melancon, 191-222. Chelsea, Mich.: Lewis Publishers, Inc.
- Wauchope, R. D., J. R. Young, R. B. Chalfant, L. R. Marti, and H. R. Sumner. 1991. Deposition, mobility and persistence of sprinkler-irrigation-applied Chlorpyrifos on corn foliage and in soil. *Pestic. Sci.* 32(2): 235-243.
- Weed, D. A. J., R. S. Kanwar, C. Cambardella, and T. B. Moorman. 1998. Alachlor dissipation in shallow cropland soil. *J. Environ. Qual.* 27(4): 767-776.
- Workman, S. R., S. E. Nokes, and L. M. McDonald Jr. 1998. Dissipation and distribution of herbicides in a Fluventic Hapludoll soil. *Environ. Sci. Technol.* 32(10): 1462-1465.
- Workman, S. R., A. D. Ward, N. R. Fausey, and S. E. Nokes. 1995. Atrazine and alachlor dissipation rates from field experiments. *Transactions of the ASAE* 38(5): 1421-1425.